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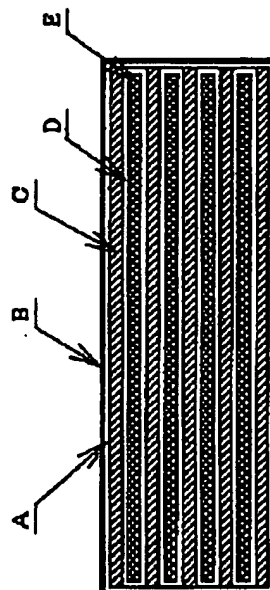
(54) SEALED BATTERY

(57) Abstract

PURPOSE: To suppress a self discharge when a battery being left in a charged state by providing a non-porous metal layer on a surface of a battery container made of a synthetic resin.

CONSTITUTION: A closed type battery comprises a battery container A made of a synthetic resin, a non-porous metal layer B, a metal hydride electrode C, a separator D, and a nickel hydroxide electrode E. In the sealed battery of this constitution, the non-porous metal layer B is provided on the external or internal surface of the battery container A made of a synthetic resin. Thereby, hydrogens permeating the battery container A made of a synthetic resin are blocked by the metal layer B, the hydrogen penetration speed of which being small. As the result, the self discharging speed of a negative electrode accompanying hydrogen generation, is decreased.

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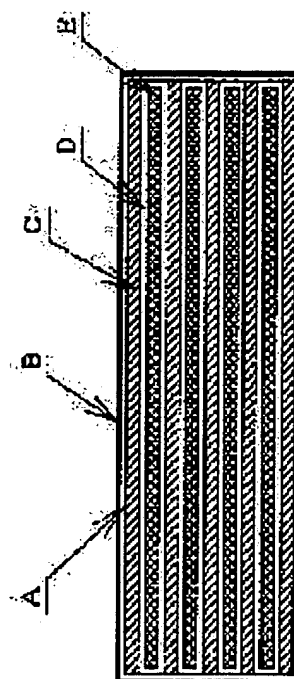
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CLAIMS

[Claim(s)]

[Claim 1] The sealing form cell characterized by coming to prepare the metal layer of the quality of nonporous in the front face of this cell container in a sealing form cell equipped with the negative electrode which makes a hydrogen storing metal alloy a subject, and the cell container made of synthetic resin.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a sealing form cell equipped with the negative electrode and the cell container made of synthetic resin which make a hydrogen storing metal alloy a subject.

[0002]

[Description of the Prior Art] There are an alkaline cell which uses a nickel hydroxide electrode, a diacid-ized manganese electrode, etc. for a positive electrode, and an acid cell which uses a lead electrode etc. for a positive electrode in the sealing form cell which uses as a negative electrode the metal hydride electrode which makes a hydrogen storing metal alloy a subject.

[0003] This metal hydride electrode uses for an electrode the hydrogen storing metal alloy in which the reversible occlusion and emission of hydrogen are possible, and uses the electrochemical oxidation reduction reaction of that hydrogen for the electromotive reaction of the negative electrode of a cell. In the hydrogen storing metal alloy used for a metal hydride electrode, it is TiNi, Ti₂ nickel, and LaNi₅. And what permuted the configuration element of intermetallic compounds, such as TiMn₂, and these intermetallic compounds by other elements is used. Since properties, such as a retention volume property if the presentations differ, in case these hydrogen storing metal alloys will repeat charge and discharge in a hydrogen storage capacity, an equilibrium hydrogen pressure, and the electrolytic solution, change, the presentation of an alloy is changed and amelioration of the engine performance of a metal hydride electrode is tried. In ordinary temperature, the hydrogen storing metal alloy whose equilibrium pressure is about 0.01 to 1 atmospheric-pressure extent is used for this electrode in many cases.

[0004] This metal hydride electrode combined the powder of these hydrogen storing metal alloys with the electrolytic-solution-proof nature macromolecule, or sintered it at the elevated temperature, and is the approach of filling up foaming metal etc., and was manufacturing the porous thing.

[0005] It is this kind of sealing form cell, and the thing made of the synthetic resin of electrolytic-solution-proof nature, such as a case where especially discharge capacity uses a metal thing for the container of the large-sized cell more than Number Ah, and an acrylic-styrene copolymerization object, polypropylene, may use. And since welding needs to perform the closure of a cell to use a metal container, it is inferior to the efficiency of the assembly operation of a cell. However, since a cell can be closed by the heating welding in low temperature farther than junction by adhesives, and metaled welding when using the cell container made of synthetic resin, it excels in the efficiency of the assembly operation of a cell. Moreover, when using the cell container made of synthetic resin, since the one molding of two or more cell containers can be easily manufactured on the group cells which consist of two or more cells, it is advantageous to it also at the point that a cell container becomes cheap.

[0006]

[Problem(s) to be Solved by the Invention] As mentioned above, when the thing made of synthetic resin was used for the cell container of a sealing form cell equipped with the negative electrode which makes

a hydrogen storing metal alloy a subject, the trouble that the self-discharge rate at the time of leaving a cell in the state of charge became large as compared with the case where a metal cell container is used was found out.

[0007] Then, also in the sealing form cell equipped with the negative electrode and the cell container made of synthetic resin which make a hydrogen storing metal alloy a subject, what has a small self-discharge rate was desired like the case where a metal cell container is used.

[0008]

[Means for Solving the Problem] This invention offers the sealing form cell which comes to prepare the metal layer of the quality of nonporous in the front face of this cell container in a sealing form cell equipped with the negative electrode and the cell container made of synthetic resin which make a hydrogen storing metal alloy a subject, in order to solve an above-mentioned technical problem.

[0009]

[Function] In the sealing form cell equipped with the negative electrode which makes a hydrogen storing metal alloy a subject, when the cell container made of synthetic resin is used, as a result of investigating the cause by which the self-discharge rate of a cell becomes large, the following thing was understood.

[0010] That is, when migration of the matter does not take place between the inside and outside of a cell container, the hydrogen partial pressure inside a cell is equal to the balanced hydrogen pressure of a hydrogen storing metal alloy, and the rate of the occlusion reaction of the hydrogen of a hydrogen storing metal alloy and the rate of release reaction become equal, it is in equilibrium, and the self-discharge of the negative electrode accompanied by generating of hydrogen does not happen. By the actual cell, since the reaction which oxidizes hydrogen in a positive electrode occurs at a small rate, a balance shifts in the direction in which the hydrogen in a cell is consumed, and a hydrogen partial pressure falls rather than balanced hydrogen pressure, consequently hydrogen is emitted by this from a hydrogen storing metal alloy, and the self-discharge of the negative electrode accompanied by generating of hydrogen happens. Since this self-discharge is a phenomenon which happens inside a cell, it happens regardless of the class of cell container. And since the rate at which hydrogen penetrates the wall of a cell container is remarkably small when using a metal thing for a cell container, the self-discharge of the negative electrode accompanied by hydrogen generating in this case originates mainly in the reaction for which hydrogen oxidizes with a positive electrode.

[0011] On the other hand, the transmission rate of the hydrogen in synthetic resin is more remarkably [than the transmission rate in a metal] large. And the hydrogen partial pressure in the atmospheric air which is the exterior of a cell container is more remarkably [than the balanced hydrogen pressure of the hydrogen storing metal alloy used for a negative electrode] small. Therefore, if the cell container made of synthetic resin is used, the rate at which the hydrogen in a cell penetrates the wall surface of a cell container, and is lost in the exterior of a cell will become remarkably large as compared with the case where a metal cell container is used. Consequently, the hydrogen partial pressure in a cell falls and the self-discharge rate of the negative electrode accompanied by generating of hydrogen becomes large.

[0012] In this invention, since the metal layer of the quality of nonporous is prepared in the front face of the exterior of the cell container made of synthetic resin, or the interior, the hydrogen which penetrates the cell container made of synthetic resin is prevented by this metal layer with a small hydrogen permeation rate, consequently there is an operation that the self-discharge rate of the negative electrode accompanied by hydrogen generating becomes small.

[0013]

[Example] This invention is explained using a drawing according to a suitable example.

[Cell (a) of this invention] drawing 1 shows the mimetic diagram of the cross section of the sealing form nickel and metal hydride battery (a) of this invention where an appearance is a rectangle and carried out the laminating of a positive-electrode plate and the negative-electrode plate by turns through the separator.

[0014] In drawing 1, A is a cell case made from an acrylic-styrene copolymerization object. B is the metal nickel layer of the quality of nonporous given to the front face of the exterior of the cell case A by the electroless deposition method. C is the metal hydride electrode of a negative electrode. D is a

separator which consists of a nonwoven fabric of the fiber of mixture with the polystyrene which sulfonated with polyethylene and granted the hydrophilic property. E is the sintering-type nickel hydroxide electrode of a positive electrode.

[0015] the thickness of the cell container A -- about 2mm -- it is -- the thickness of deposit B of metal nickel -- about 100 micrometers it is .

[0016] The weight of the sum total of the nickel hydroxide contained in four sheets of the nickel hydroxide electrode E of a positive electrode is 39g per one cel. Therefore, when nickel hydroxide assumes following 1 electronic reaction, the geometric capacity of the positive electrode of one cell is about 11 Ah(s). In this electrode, 0.04g of cobalt hydroxide per 1g of nickel hydroxide is added.

[0017] The negative-electrode plate C was manufactured as follows.

[0018] For a hydrogen storing metal alloy, the presentation is $\text{LaNi}_{3.8}\text{Co}_{0.7}\text{Al}_{0.5}$ at an atomic ratio. It ground, after dissolving and casting the configuration element all over the high frequency induction furnace made into the vacuum in the state of the metal so that it might become. La is about 90 % of the weight about La here. It is the lanthanum rich misch metal which is the mixture of the rare earth metal to contain. It distributed in the water solution of the polyvinyl alcohol which achieves the function of a thickener and a binder, and this alloy powder was made into the shape of a paste. And both sides of the iron punching metal which performed nickel plating were plastered with this paste, it dried, pressed and cut to them, and the metal hydride electrode was manufactured.

[0019] The weight of the hydrogen storing metal alloy contained in five negative-electrode plates of this one cell is about 53g.

Cell (b) of [cell (b) of this invention] this invention carried out heat welding, made other configurations the same as cell (a), and manufactured the film which laminated the aluminum foil of the quality of nonporous of the same thickness with polypropylene and a vinylidene-chloride-resin film instead of deposit B of the metal nickel of the quality of nonporous in cell (a) of this invention.

Without preparing deposit B of the metal nickel in cell (a) of this invention, other configurations were made the same as cell (a), and cell (c) of the [conventional cell (c)] former manufactured them.

[Experiment] In these sealing form nickel and metal hydride batteries, it is ZnO of 0.4M. 10 g/l KOH of the concentration of 6M which dissolved LiOH The electrolytic solution which consists of a water solution is poured in tales doses every.

[0020] formation of discharging with the current of the rate of 5 time amount after charging the above sealing form nickel and metal hydride battery with the current of the rate of 10 time amount on the basis of the geometric capacity of a positive electrode for 16 hours -- charge and discharge were performed twice.

[0021] Next, it charged with the current of the rate of 10 time amount for 15 hours, and the discharge capacity before neglect was measured on the conditions of discharging until terminal voltage is set to 1V with the current of the rate of 5 time amount. And the discharge capacity after neglect was measured on the conditions of discharging after charging for 15 hours and leaving it for 20 days with the current of the rate of 10 time amount until terminal voltage is set to 1V with the current of the rate of 5 time amount. These charges and discharges were performed in the ambient temperature of 25 degrees C, and the charged cell was left at 40 degrees C.

[0022] In this trial, the capacity retention by neglect is defined as the discharge capacity after the neglect to the discharge capacity before neglect, and the value of the capacity retention of each cell obtained by the above-mentioned trial is shown in Table 1.

[0023]

[Table 1]

電 池	40℃20日後の 容量保持率(%)
(ア)	68
(イ)	70
(ウ)	35

It is in ** that it is remarkable, and is high, therefore a self-discharge rate is remarkable, and cell (a) of Table 1 to this invention and the capacity retention of (b) are small as compared with conventional cell (c).

[0024] In addition, although the above-mentioned example described the case of the alkaline battery which uses a sintering-type nickel hydroxide electrode for a positive electrode, the electrode with which the positive electrode filled [the electrolytic solution] up nickel hydroxide with the alkali water solution into a nickel fiber sintered compact or foaming nickel, the case where positive active material is diacidized manganese, a silver oxide, and peroxidation silver, and the electrolytic solution do so the operation effectiveness as the above-mentioned example that it is the same also when positive active material is lead peroxide, by aqueous acids. However, when the electrolytic solution is acidity, since corrosion resistance is low, it is desirable [the hydrogen storing metal alloy of the above-mentioned example] to use the amorphism alloy of a presentation which is indicated by JP,61-269854,A, for example.

[0025] Moreover, although the above-mentioned example explained the case where the thing of a specific presentation was used as a hydrogen storing metal alloy of a negative electrode As for the operation effectiveness of this invention, the hydrogen in a hydrogen storing metal alloy and the cell in equilibrium penetrates the cell container made of synthetic resin. Since it controls being lost out of a cell with a low hydrogen partial pressure by the metal layer with the slow passing speed of hydrogen, the presentation of the hydrogen storing metal alloy of the negative electrode of a cell for which the means of this invention does the operation effectiveness so is not limited to the thing of the above-mentioned example.

[0026] Furthermore, the above-mentioned example explained the case where the electroless deposition layer of nickel or the laminate film of aluminum was used, as a metal layer of the quality of nonporous. However, since the same operation effectiveness is done so also when using chromium, copper, etc. if it considers as the quality of the material of a metal layer in addition, the quality of the material of the metal layer in this invention is not limited to what is indicated in the example. Moreover, approaches, such as vacuum deposition, electroplating, and thermal spraying, are also applicable as a means to prepare the metal layer of the quality of nonporous.

[0027] And even if the part in which the metal layer of the quality of nonporous is prepared is not only the outer surface of a cell container but the inner surface, it can acquire the same operation effectiveness as the above-mentioned example. However, in this case, it is necessary to adopt an insulating means as the positive electrode and negative electrode in a cell do not short-circuit through this metal layer. Moreover, when this metal layer prepared in the inner surface of a cell container touches the electrolytic solution, in not the metal that is inferior to the corrosion resistance over an acid or the alkali electrolytic solution like aluminum but the alkali electrolytic solution, nickel is suitable, and lead is suitable in the acid electrolytic solution.

[0028]

[Effect of the Invention] According to this invention, the effectiveness that the self-discharge at the time of leaving the cell of a charge condition is controlled is done so.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The mimetic diagram of the cross section of the sealing form nickel and metal hydride battery (a) of this invention where the appearance carried out the laminating of a positive-electrode plate and the negative-electrode plate by turns through the separator with the rectangle.

[Brief Description of Notations]

- A The cell container made of synthetic resin
- B Nature metal layer of nonporous
- C Metal hydride electrode
- D Separator
- E Nickel hydroxide electrode

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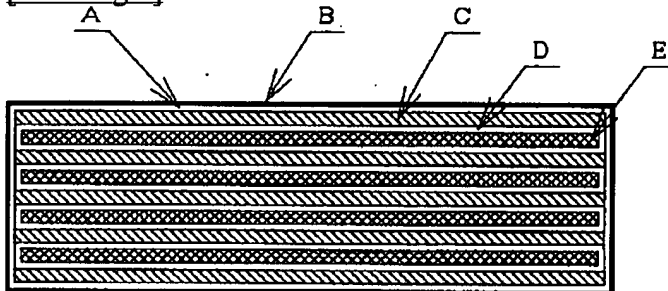
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DRAWINGS

[Drawing 1]



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